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Swelling of EPDM rubbers for oil-well applications as influenced by medium composition and temperature
II. Experimental part

The first part of the paper describes the mechanism of interactions between hydrocarbon solvents and vulcanized rubber (representing crosslinked network structure). The problem has been discussed from the point of view of thermodynamic principles of swelling, temperature and material factors affecting swelling of filled rubber vulcanizates, as well as the impact of swelling on properties of the materials. In the second part of the paper results of own research, devoted to swelling of sulphur vulcanizates of EPDM rubber in hydrocarbon solvents contained in mineral oils and fuels, or their mixture. Using headspace Gas Chromatography, the degree of swelling rubber vulvanizes by different components of solvent mixture in a function of temperature, has been determined.

Keywords: EPDM, hydrocarbon solvents, solubility parameter, swelling.

Wpływ oleju i temperatury na pęcznienie gumy EPDM do zastosowań w szybach naftowych
II. Część doświadczalna

Pierwsza część artykułu przedstawia mechanizm oddziaływania między rozpuszczalnikami węglowodorowymi a usieciowanym kauczukiem (reprezentującym usieciowaną strukturę przestrzenną). Zagadnienie zostało przedyskutowane z punktu widzenia podstawowych praw termodynamiki dotyczących rozpuszczalności, temperatury i czynników materiałowych, mających wpływ na oddziaływanie rozpuszczalników na napełnione wulkanizaty oraz wpływu na ich właściwości. W drugiej części artykułu przedstawiono wyniki badań własnych, dotyczących pęcznienia nienapełnionych, siarkowych wulkanizatów EPDM w węglowodorowych rozpuszczalnikach wchodzących w skład olejów mineralnych i paliw, oraz w ich mieszaninie. Za pomocą chromatografii gazowej, z zastosowaniem metody headspace, oznaczono stopień spęcznienia wulkanizatów kauczuku przez różne składniki mieszaniny rozpuszczalników w funkcji temperatury.

Słowa kluczowe: EPDM, rozpuszczalniki węglowodorowe, parametr rozpuszczalności, pęcznienie.

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Introduction

This is the second manuscript / continuation of a first one covering the use of EPDM rubbers for swelling applications in oil-well packers. The first covered the theoretical background of swelling of rubbers in various media and has been published in an earlier issue of *Elastomery* journal [1].

4. Experimental

4.1. Materials involved in this study

4.1.1. EPDM rubber

EPDM (Ethylene Propylene Diene polyMethylene rubber) compounds are widely used in industrial applications, where its main advantage over Styrene-Butadiene (SBR), Isoprene (IR), Butadiene (BR) rubbers and Natural Rubber (NR) is the high temperature and ozone stability. EPDM rubber is capable to be extended with fillers and plasticizers to a very high level in comparison with the other elastomers mentioned above, and still give good processability and properties in articles [2]. EPDM is a hydrocarbon polymer, which swells excessively in hydrocarbon fluids such as mineral oils and hydrocarbon fuels, because of lack of polar groups in the polymer chain. An example of its swelling behavior is presented in Table 1.

Table 1. Example of swelling behavior of EPDM vulcanizates in hydrocarbon fluid [3]
Tabela 1. Przykładowe efekty pęcznienia wulkanizatów EPDM w oleju mineralnym [3]

Elastomer base	EPDM (hydrocarbon rubber)
Medium	Hydrocarbon oil with low aniline point (at 70 °C)
Test temp. [°C]	100
Test duration [h]	168
Original hardness [Shore A]	50
Change in Shore A hardness [points]	−30
Volume change [%]	185

EPDM is a synthetic elastomer with low modulus, low tensile stress and high elongation at break, which is tough and oleophilic [4]. It is interesting also due to good flexibility at low temperatures and resistance to acids, alkalis and oxygenated solvents. EPDM consists of macromolecules containing double bonds outside the polymer backbone, which accounts for its ozone-resistance, but its cross-linking effect is much weaker than that of general purpose rubbers due to the low concentration of crosslinking sites [5].

The general formula of EPDM is given in Figure 6, where (in case of EPDM used in the present investigation) $x \approx 48$ wt. %, $y \approx 48$ wt. %, $z \approx 4$ wt. % for an average amorphous EPDM, wherein the co-monomers are statistically distributed along the molecular chain [2].
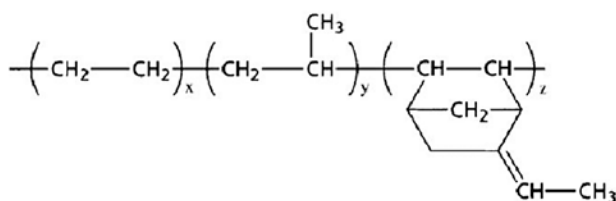

Fig. 6. EPDM polymer structure with ENB units [6]
Rys. 6. Struktura polimeru EPDM zawierającego mery ENB [6]

The rubbery properties of ethylene–propylene copolymers are exhibited over a broad range of compositions, but weight percentages of commercial products generally range from 45 : 55 to 80 : 20 wt. % ethylene/propylene. With increasing propylene content, the polymer loses thermal and ozone stability, because of the lower oxidative stability of the methyl-groups in the propylene units relative to the ethylene units. With a high ethylene content, the polymer becomes too crystalline and loses its rubbery character [2].

EPDM includes carbon-carbon unsaturation, pendent to the main chain, of a small amount of an appropriate third diene monomer to make it suitable for conventional sulfur vulcanization chemistry. A characteristic of the structure of commercially used third monomers is that the two double bonds are non-conjugated. These are cyclic and bicyclic dienes with a bridged ring system. The most commonly used third monomer is 5-ethylidene-2-norbornene (ENB) which is polymerized into the ethylene–propylene chain to give poly(ethylene-*co*-propylene-co-ENB): Figure 6. The norbornene double bond in the bridged, or strained ring is the more active with respect to polymerization and the five-membered ring is left with the double bond as a pendent substituent to the main polymer chain [6].

Selection of the appropriate cure system is dependent on the final properties desired. For EPDM either sulfur cure systems or organic peroxides can be used for vulcanization. With the sulfur cure system crosslinking occurs at the pendant carbon-carbon double bond. Common accelerators such as thiazoles, thiurams, and dithiocarbamates are used together with elemental sulfur or an organic sulfur compound [7]. The methyl-groups in the propylene units inhibit crosslinking reactions with

peroxides, and instead can lead to too much chain scission in high propylene-containing EPDM's. Consequently, copolymers of propylene and ethylene can be crosslinked with peroxides if the ethylene concentration is sufficiently high. Therefore, if peroxide cures and high degrees of crosslinking are required, the EPDM should have at least 50 mole% of ethylene well distributed along the polymer chain [8]. Organic peroxides are recommended for EPDM applications where heat resistance and lowest compression set are important requirements. The principal site for crosslinking is at or near the side-chain double bond on the diene. The rate and state of cure are dependent on the type of diene used in the polymer [7]. A third method for vulcanization of EPDM is the use of halogenated polymethylol resin, where formation of a benzyl-carbonium-ion from methyl groups of the resin occurs. Zinc oxide reacts with the halogen from the resin or from another source such as chlorinated rubber or $SnCl_2 \cdot 2H_2O$, and then catalyzes the reaction between the resin and the $-C=C-$ unsaturation on the polymer to form crosslinks. This approach is considered for extreme heat and compression set resistance and for high temperature curing stability [7].

4.1.2. Crude oil components

Petroleum (crude oil) is a complex mixture of paraffinic, naphthenic and aromatic hydrocarbons ranging in carbon number from C_1 till C_{60}, with smaller amounts of heteroatom compounds, metals either complexed with porphyrins or as salts of carboxylic acids, and hydrogen sulfide. It is not a uniform substance since its physical and chemical properties vary from oilfield to oilfield and can even vary within wells at the same oilfield [9]. The crude oil quality varies from a light, mobile, straw-colored liquid to a highly viscous, semi-solid, black substance. The lower molecular weight components of petroleum show moderate to high water solubility and have a high vapor pressure, while the higher molecular weight fractions tend to form emulsions in water and have negligible to low vapor pressure. The lighter weight aliphatic and aromatic components of petroleum have high mobility in soil while the heavier molecular weight constituents possess low mobility.

The vapor pressure is moderate to high for most constituents of petroleum. The rate of hydrolysis is negligible since the paraffins, naphthenes and aromatic hydrocarbons contained in petroleum do not possess functional groups that hydrolyze under environmental conditions. The rate of atmospheric photooxidation is slow to rapid for most components of petroleum [9].

The chemical components of crude oil are hydrocarbon compounds containing only carbon and hydrogen atoms, and organic compounds containing in addition atoms such as sulfur, oxygen or nitrogen to represent a group of non-hydrocarbon components.

Petroleum hydrocarbons include the following compounds:
- *n*-paraffins (*n*-alkanes) with general formula C_nH_{2n+2};
- isoparaffins (*iso*-alkanes) with general formula C_nH_{2n+2}, including highly branched hydrocarbons;
- naphthenic (cycloparaffins, cycloalkanes), mainly monocyclic, with general formula C_nH_{2n}, such as cyclopentane, cyclohexane, also two- or more (up to 10) rings of naphthenes with (or without) alkyl substituents. It is the most numerous group of hydrocarbons in crude oil (average 50%);
- aromatics (around 15%), which contain mostly methylbenzene and its derivatives (benzene, toluene, ethylbenzene, xylenes) and alkylbenzenes having up to 40 carbon atoms in the substituents. The crude oil contains also polycyclic aromatic hydrocarbons (PAH) containing from 2 (naphthalene) to 10 fused rings;
- around 5% are mixed structures containing both aromatic rings and naphthenic moieties, for example indan, tetralin, acenaphthene [9].

Hydrocarbons have a nonpolar character. As an example, some of the compounds occurring in petroleum and their basic characteristics are presented in Table 2.

4.2. Samples preparation

The experiments were done with using unfilled (non-reinforced) Low Mooney EPDM rubber supplied by Lanxess Elastomers B.V, the Netherlands, mixed in a Toshin TD3–10MDX laboratory dispersion mixer, vulcanized with sulfur and accelerators, pressed into sheets with a thickness of about 2 mm in a Jing Day laboratory press for 30 minutes at a temperature of 160 °C. From the sheets 3 samples for each mixture with weight 0.100±0.010 g were cut. The density of the unswollen samples at room temperature, determined by weighting in air and water was: 0.913 ± 0.001 g/cm³.
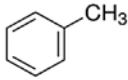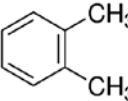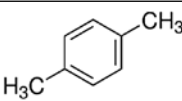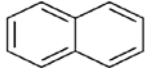
4.3. Mixture characteristics
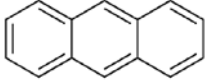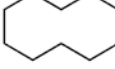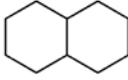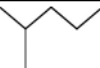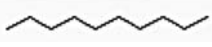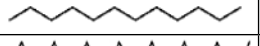
Among the compounds present in the crude oil, 14 representative species from the naphthenic, paraffinic and aromatic components were selected to carry out swelling tests at room temperature: Table 3. Three of them: *o*-xylene, cyclooctane and dodecane were used to perform swelling test investigations at higher temperatures: 40, 60 and 80 °C, besides swelling at room temperature. Those three representative liquids were investigated at different temperatures as pure liquids as well as mixed in different proportions: Table 4, to study the influence of mixing of particular components on

solvent absorption. Characterization of all 14 liquids with respect to density, molar mass, molar volume, structure and solubility parameter, taken from 2 different sources: i.e. MOSCED (Modified Separation of Cohesive Energy Density) [10], and HSP (Hansen Solubility Parameter) [11], are also given in Table 3.

All 14 representative liquids will be treated in detail in paper III of this series, to characterize the effect of molar volume of the liquids on swelling; selections out-of those 14 were used for the characterization of the solubility parameter of EPDM-rubber in the present manuscript II of this series.

Table 2. The basic characteristics of the main components of crude oil [9, 12]
Tabela 2. Podstawowa charakterystyka głównych składników ropy naftowej [9, 12]

Name	Structural formula	Temperature [°C]				Viscosity
		Boiling*	Melting**	Auto-ignition***	Flash****	at 20 °C [cP=mPa·s]
Aromatic						
toluene		111	−95	480	6	0.590
o-xylene		136	−25	463	31	0.812
p-xylene		144	13	530	25	0.648
naphthalene		218	80	526	80	0.780 (at 90 °C)
anthracene		340	218	540	121	0.501 (at 245 °C)
Cycloparafinic/Naphthenes						
cyclohexane		80	7	245	-18	1.020
cyclooctane		149	13	290	29	1.890
cyclodecane		201	10	290	65	1.471
cis-decalin		193	−43	255	58	1.930
trans-decalin		185	−31	250	52	
Isoparaffinic						
2-methylpentane		60	−146	306	−7	0.306
pristane		296	−99	595	110	5.102
***n*-Paraffinic**						
n-decane		174	−30	210	46	0.638
n-dodecane		216	−10	203	71	1.503
n-hexadecane		280	18	215	135	3.340

*The boiling point of a substance is the temperature at which the vapor pressure of the liquid equals the pressure surrounding the liquid (atmospheric pressure) and the liquid changes into a vapor.
**The melting point of a solid is the temperature at which it changes from solid to liquid state at atmospheric pressure.
***The autoignition temperature of a substance is the lowest temperature at which it will spontaneously ignite at normal atmospheric conditions without an external source of ignition, such as a flame or spark.
****The flash point of a volatile material is the lowest temperature at which it can vaporize to form an ignitable mixture in air.

Table 3. Characteristics of representative aromatic, naphthenic and paraffinic structures contained in crude oil
Tabela 3. Charakterystyka reprezentatywnych struktur aromatycznych, naftenowych i parafinowych, pochodzących ze składników ropy naftowej
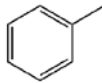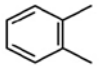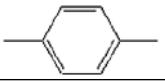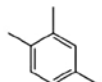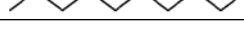
Liquid	Molar mass [g/mol]	Density [g/cm³]	Molar volume [cm³/mol]	Structure	MOSCED δ_s [10] [MPa$^{1/2}$]	HSP δ_s [11] [MPa$^{1/2}$]
AROMATIC						
benzene	78.11	0.874	89.37		17.91	18.51
toluene	92.14	0.867	106.27		17.60	18.16
o-xylene	106.16	0.879	120.77		17.93	18.10
p-xylene	106.15	0.861	123.29		17.50	17.70
cumene	120.19	0.864	139.11		17.90	17.95
1,2,4-trimethylbenzene	120.19	0.876	137.20		–	18.06
NAPHTHENIC						
cyclopentane	70.10	0.751	93.34		16.40	16.50
cyclohexane	84.16	0.779	108.04		16.80	16.80
cyclooctane	112.21	0.834	134.54		17.50	17.50
PARAFFINIC						
n-pentane	72.15	0.630	114.52		15.30	14.40
n-hexane	86.18	0.659	130.77		15.70	14.90
n-heptane	100.21	0.683	146.72		16.00	15.30
n-decane	142.29	0.730	194.92		16.50	15.70
n-dodecane	170.33	0.750	227.11		16.70	16.00

Table 4. Various pure solvents investigated and composition of their mixtures
Tabela 4. Skład badanych cieczy i ich mieszanin

Mixture number	*o*-Xylene [%]	Cyclooctane [%]	Dodecane [%]
I	100	0	0
II	0	100	0
III	0	0	100
IV	33	33	33
V	75	25	0
VI	75	0	25
VII	50	50	0
VIII	50	0	50
IX	0	50	50
X	25	75	0
XI	25	0	75
XII	0	75	25
XIII	0	25	75
XIV	50	25	25
XV	25	50	25
XVI	25	25	50

4.4. Details of experiments

4.4.1. Swelling tests

Each of the samples was weighed in air and water before immersion in a liquid, then the thickness and diameter were measured. The samples were immersed in an excess of liquid (20 ml). To measure changes with time, the immersed samples were periodically removed from the liquid at intervals of 1, 3, 5, 7, 28, 48, up to 96 hours (to determine equilibrium swelling) and excess solvent was wiped off quickly using a paper cloth. The samples were then weighed and their dimensions measured, followed by immediately placing the samples back in the fluid. The time taken for each set of measurements was kept to a minimum: approximately 60 seconds. The increase in weight of rubber was taken as the weight of liquid absorbed.

The procedure was the same for the 4 temperatures: 22, 40, 60, 80 (±3) °C. When conducting the experiments at temperatures higher than room temperature, the samples were kept in a thermostatically controlled air oven. Swelling ratios Q and then volume fractions of polymer in the swollen mass v_r for different temperatures were determined using Equations (11) and (12) as given in manuscript I of this series.

4.4.2. Density determination

4.4.2.1. Density of rubber

The density of the samples was examined by immersion in water with an analytical balance at 20 °C, based on the Archimedes principle, which states that a body immersed in a liquid loses weight as much as the weight of the displaced fluid. The buoyant force is equal to the weight of the displaced fluid. The density of solid rubber was obtained from the weight of the sample in air (m_{air}), the weight in water (m_{water}) and the density of water (d_{H_2O}) at the temperature of the experiment (Table 6, see later) and can be found by:

$$d_r = \frac{m_{air}}{m_{air} - m_{water}} \cdot d_{H_2O} \qquad (27)$$

where d_r is the density of the rubber sample. The final value is an average of 16 separate measurements.

4.4.2.2. Density of swelling liquids

The liquid densities were determined with a pycnometer. Using a reference fluid with well-known density such as distilled water, for which temperature dependent values of the density are shown in Table 5,

it is possible to obtain the density of another liquid. The pycnometer (Figure 7) is a glass flask with a close-fitting ground glass stopper with a capillary hole through it. This fine hole releases spare liquid after closing a top-filled pycnometer and allows for obtaining a given volume of measured and/or working liquid with high accuracy [13].

Fig. 7. Pycnometer with thermometer
Rys. 7. Piknometr z termometrem

First the mass of empty dry pycnometer (m_p) with thermometer and stopper is measured, then of the filled pycnometer with distilled water (m_{H_2O}) at 20 °C. To determine the density of the unknown liquid, the weight of pycnometer filled with this liquid (m_L) is measured at 20 °C. The densities of the liquids were then determined using the following equation:

$$d_L^{20} = \frac{m_L - m_p}{m_{H_2O} - m_p} \cdot d_{H_2O}^{20} + \beta \qquad (28)$$

where d_L^{20} is the density of the liquid at 20 °C in g/cm³, $d_{H_2O}^{20}$ is the density of water at 20 °C in [g/cm³], and β is a correction for weighing in air and equals 0.0012. The final values are averages of 3 measurements.

Table 5. Temperature dependence of distilled water density d_{H_2O} [14]
Tabela 5. Zależność gęstości wody destylowanej od temperatury d_{H_2O} [14]

T [°C]	d_{H_2O} [kg/m³]
15	999.0986
16	998.9420
17	998.7739
18	998.5946
19	998.4043
20	998.2033
21	997.9918
22	997.7700
23	997.5382
24	997.2964
25	997.0450

4.4.3. Headspace gas chromatography

Headspace is a gas space above the sample in a chromatographic vial. Volatile sample components diffuse into the gas phase, forming the headspace gas. Headspace analysis is therefore the analysis of the components present in that gas. In the present case, swollen rubber was used to determine the amount of each component present in the swollen sample. Each of the samples was weighed in air before immersion in a liquid and then left in that liquid for minimum 96 hours. After this time the swollen rubber samples were dried with a paper cloth, weighed and put into a gas chromatography (GC) vial of 20 ml size, and then put in the GC tray. To prepare calibration lines, series of mixtures were prepared with concentrations of 100 : 0, 90 : 10, 80 : 20, 60 : 40, 40 : 60, 20 : 80 for mixtures of *o*-xylene : cyclooctane, *o*-xylene : dodecane and dodecane : cyclooctane, respectively. The volume of a liquid in the vial and in the swollen rubber samples was around 20–30 µl.

An Agilent 7890A Gas Chromatograph with 5975C Mass Spectrometer was used in this investigation. The gas-tight syringe technique operates by initially thermostatting the sample in an incubation oven at a given temperature (200 °C) and for a given time until it has reached a state of equilibrium (5 minutes). Once the sample has reached equilibrium, an aliquot is taken from the headspace using the gas-tight syringe, and the aliquot is injected into the GC. In order to customize the method of injection of gas onto the chromatography column for a given mixture of liquids, a series of measurements were done and finally the injection volume was set as 250 µl with split 1 : 500.

5. Results and discussion

5.1. Swelling test results

According to the procedure described in Chapter 4.4.1, the liquid mass uptake at equilibrium and then the volume fractions of polymer in the swollen masses v_r: Table 6, for different temperature, were determined with using Equations (11) and (12) (see Chapter 3.1 in manuscript I), and for temperature above 22 °C the densities and molar volumes were obtained using the thermal expansion coefficients according to Table 10 (see later).

Table 6. Volume fractions of EPDM elastomer in swollen mass at different temperature
Tabela 6. Kinetyka pęcznienia objętościowego wulkanizatu EPDM w wybranych rozpuszczalnikach

Mixture number	*o*-Xylene	Cyclooctane	Dodecane	22 °C		40 °C		60 °C		80 °C	
				Mass change [%]	$v_r\,20$	Mass change [%]	$v_r\,40$	Mass change [%]	$v_r\,60$	Mass change [%]	$v_r\,80$
I	100	0	0	310	0.23	320	0.22	310	0.23	310	0.23
II	0	100	0	400	0.18	400	0.18	400	0.18	400	0.18
III	0	0	100	250	0.25	240	0.25	240	0.25	250	0.25
IV	33	33	33	330	0.21	320	0.22	310	0.21	320	0.21
V	75	25	0	370	0.20	350	0.21	330	0.22	330	0.22
VI	75	0	25	330	0.22	320	0.22	320	0.22	310	0.22
VII	50	50	0	400	0.19	380	0.20	360	0.20	380	0.19
VIII	50	0	50	310	0.22	290	0.23	290	0.23	300	0.22
IX	0	50	50	330	0.21	310	0.22	300	0.22	290	0.22
X	25	75	0	420	0.18	380	0.19	370	0.19	380	0.19
XI	25	0	75	290	0.23	260	0.24	260	0.24	260	0.23
XII	0	75	25	370	0.19	350	0.20	340	0.20	340	0.16
XIII	0	25	75	290	0.23	270	0.24	270	0.24	260	0.23
XIV	50	25	25	360	0.20	330	0.21	330	0.21	330	0.21
XV	25	50	25	350	0.20	350	0.20	340	0.20	350	0.20
XVI	25	25	50	320	0.21	300	0.22	300	0.22	300	0.22

The higher the swelling ratio and absorption, the lower v_r. However, no systematic trend can be seen between the different temperatures. The changes of swelling ratio at higher temperature relate to changes in solubility parameters of the rubber and the liquids. Those differences are discussed later.

Table 7. Swelling test results in selected solvents taken from 3 different parts of elastomer sheets
Tabela 7. Wyniki oznaczeń pęcznienia wulkanizatu EPDM dla 3 próbek pobranych z różnych miejsc płytek

Solvent	Longer edge [%]	Middle [%]	Shorter edge [%]	Average [%]
o-xylene	310	318	314	314
cyclooctane	402	404	407	404
dodecane	255	257	248	253

All samples were prepared with the assumption that the crosslinking does not vary across the thickness of the vulcanized sheets. To verify this, tests were done by taking samples from the short and long edges as well as from the middle of the elastomer sheets. The results given in Table 7 show no significant changes in the percent swelling for samples taken from the edge compared with those taken from the middle part. The small deviations could be an effect of inaccuracies in the measurements or small differences in crosslink density between different parts of the elastomer sheet.

In some cases maximal solvent uptake is reached and then this value reduces slightly, as shown in Table 8. Brandt–Nielsen and Hansen [15] in their investigation of EPDM rubber observed this behavior as well and reported, that it can be caused by low molecular weight polymer which is not incorporated in the elastomer network by vulcanization and leaches out of the sample into the liquid.

5.2. Density

According to the procedure described in Chapter 4.4.2.1, an exemplary density of EPDM rubber sample was determined using Equation (29):

$$d_r = \frac{1.570\,\text{g}}{1.716\,\text{g}} \cdot 0.998\,\frac{\text{g}}{\text{cm}^3} = 0.913\,\frac{\text{g}}{\text{cm}^3} \qquad (29)$$

To calculate swelling ratios, the densities of liquids were determined using the pycnometer. An exemplary density for *o*-xylene according to the method described in 4.3.2.2 using Equation (30) amounts to:

$$d_{o\text{-xylene}}^{20} = \frac{88.7259\,\text{g} - 44.4540\,\text{g}}{94.7588\,\text{g} - 44.4540\,\text{g}} \cdot 0.9982\,\frac{\text{g}}{\text{cm}^3} + 0.0012\,\frac{\text{g}}{\text{cm}^3} \cong 0.880\,\frac{\text{g}}{\text{cm}^3} \quad (30)$$

Densities of mixtures of liquids were also calculated, based on literature values of densities for the pure components *o*-xylene, cyclooctane and dodecane using the following equation:

$$d_1 = d_{s1}v_{s1} + d_{s2}v_{s2} + d_{s3}v_{s3} \qquad (31)$$

where d_1 is the density of the mixture of liquids, and d_{s1}, d_{s2}, d_{s3}, v_{s1}, v_{s2}, v_{s3} are the densities and volume fractions of *o*-xylene, cyclooctane and dodecane, respectively.

Densities of liquids obtained from both methods are comparable: Table 9. The small differences can be the result of inaccuracy of the measurements.

The volume of an object increases with increase in temperature because of volumetric thermal expansion. Data for thermal expansion coefficients of liquids are presented for major organic chemicals in [16]. They recommend the following equation for correlation of the thermal expansion coefficient of a liquid and temperature:

$$\beta_{\text{liq}} = a \cdot \left(1 - \frac{T}{T_c}\right)^m \qquad (32)$$

where β_{liq} is the thermal expansion coefficient of the liquid [1/K], a and m are regression coefficients for chemical compounds, T is temperature [K], and T_c is a critical temperature [K]. The results for thermal expansion coefficients are given in Table 10 for *o*-xylene, cyclooctane and dodecane [16]. The presented values are applicable to a wide variety of substances. The table also discloses the temperature range for which the equation is useable. The respective minimum and maximum temperatures are denoted by T_{min} and T_{max}.

Table 8. Solvent mass uptake changes by EPDM vulcanizate during time for selected solvents
Tabela 8. Kinetyka pęcznienia wagowego wulkanizatu EPDM w wybranych rozpuszczalnikach

Solvent	Time [hours]						
	1	3	5	7	24	48	96
o-xylene [%]	160.71	270.42	303.72	313.07	315.45	315.23	314.40
cyclooctane [%]	103.95	215.48	293.20	336.56	403.47	405.15	404.37
dodecane [%]	70.24	142.91	189.19	214.25	253.19	253.16	252.63

Table 9. Comparison of densities of solvent mixtures based on data from literature and experiments
Tabela 9. Porównanie gęstości mieszanin rozpuszczalników na podstawie danych literaturowych i uzyskanych doświadczalnie

Mixture number	Density calculated [g/cm³]	Density obtained by pycnometer [g/cm³]
I	0.879	0.880
II	0.834	0.837
III	0.750	0.749
IV	0.813	0.816
V	0.868	0.869
VI	0.847	0.849
VII	0.857	0.856
VIII	0.815	0.815
IX	0.792	0.793
X	0.845	0.846
XI	0.782	0.783
XII	0.813	0.815
XIII	0.771	0.772
XIV	0.836	0.837
XV	0.824	0.825
XVI	0.803	0.803

Table 10. Volumetric thermal expansion coefficient of solvents [16]
Tabela 10. Objętościowy współczynnik rozszerzalności termicznej rozpuszczalników [16]

Name	$a \cdot 10^{-4}$	T_c [K]	m	T_{min} [K]	T_{max} [K]	$\beta_{liq} \cdot 10^{-4}$ [1/K]		
						40 °C	60 °C	80 °C
o-xylene	5.844	630.37	−0.7259	247.98	598.85	9.62	10.08	10.61
cyclooctane	5.764	647.20	−0.7143	287.60	614.84	9.24	9.66	10.12
dodecane	6.067	658.20	−0.7104	263.57	625.29	9,60	10.01	10.47

5.3. Comparison of the change in mass and volume swelling

In Figure 8, the percentages increase in mass and volume of samples swollen in pure *o*-xylene, cyclooctane and dodecane are plotted as function of exposure time in those liquids. For each sample, the changes in volume are larger than the changes in mass for a given exposure time because the densities of *o*-xylene ($d_{o\text{-xylene}}$ = 0.880 [g/cm³]), cyclooctane ($d_{cyclooctane}$ = 0.837 [g/cm³]) and dodecane ($d_{dodecane}$ = 0.749 [g/cm³]) are lower than that of the elastomer (d_{rubber} = 0.913 [g/cm³]), and so the diffused liquids reduce the effective density of
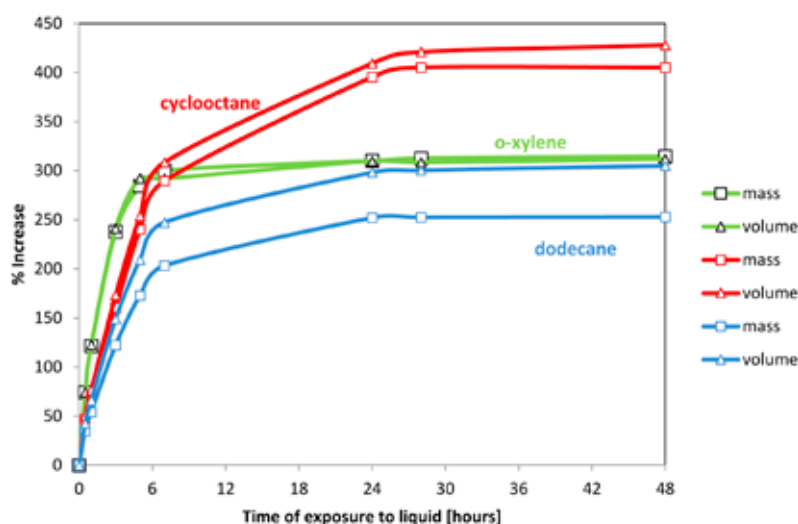

Fig. 8. Percent increase in mass and volume of EPDM rubber sample vs. time in pure *o*-xylene, cyclooctane and dodecane at room temperature
Rys. 8. Kinetyka procentowego przyrostu masy i objętości próbki wulkanizatu EPDM spęcznianej w *o*-ksylenie, cyklooktanie lub dodekanie, w temperaturze pokojowej

the swollen elastomer. The lower the density of the liquid, the larger the difference between volume and mass increase, i.e. for rubber swollen in *o*-xylene this difference is the smallest.

5.4. Accurate determination of the solubility parameter of EPDM rubber

The solubility parameter of polymers can be determined from swelling data obtained in a series of solvents covering a range in solubility parameters themselves. It can only be determined indirectly and may be affected by variations in the chemical constitutions of the polymers: the number of crosslinks per unit volume and the distribution of chain branches of substituted groups along the polymer backbones. In the case of EPDM, the main polymer in the context of this study, the ethylene/propylene ratio and the amount and type of third monomer, needed for sulfur vulcanization, play an important role.

Table 11. Comparison of solubility parameter of unvulcanized EPDM rubbers with different concentrations of 5-ethylidene-2-norbornene (ENB); ethylene and Mooney viscosity, taken from literature sources
Tabela 11. Porównanie parametrów rozpuszczalności kauczuków EPDM o różnej zawartości 5-etylideno-2-norbornenu (ENB); zawartość merów etylenowych i lepkość zaczerpnięte ze źródeł literaturowych

EPDM	ML (1+4) at 125 °C	Solubility parameter of EPDM rubber [MPa$^{1/2}$]
ENB 9.0%, ethylene 48% wt.	65	16.40 [17]
ENB 9.0%, ethylene 55% wt.	46	15.95 [18]
ENB 4.9%, ethylene 50% wt.	20	17.51 [15]
ENB 5.5%, ethylene 55% wt.	80	17.80 [15]

Table 11 shows various values for the solubility parameter of EPDM rubber taken from literature. It is clearly seen that the value depends on the composition of the EPDM and the source from where these values were obtained. Brandt-Nielsen and Hansen [15] observed that for EPDM rubber the level of branching or molecular weight, and consequently the Mooney viscosity, do not have a significant effect on the solubility of the rubber, as they obtained a Hansen solubility parameter for low Mooney un-vulcanized EPDM around 17.5 [MPa^{½}].

In the present manuscript, an attempt is made to design a possible method for an accurate determination of the

solubility parameter of the EPDM rubber-sample used throughout the study, based on swelling data in 8 of the 14 solvents mentioned in Table 3, and making use of the Flory–Rehner equation which connects the results from swelling tests with interactions between the solvents and the polymer. The weights of the samples before swelling, and the weights of the samples at equilibrium swelling were taken to calculate the volume fractions of polymer in the swollen mass v_r as shown in Table 12. These results, together with the respective molar volumes v_s – see also Table 3 – and solubility parameters of the solvents δ_s, were used to calculate from the Flory–Rehner Equation (10 in the first paper [1]) the concentration of elastically active chains per unit volume of polymer, v_e. Table 12 presents also values for the solubility parameters, dependent on the source of data: taken from MOSCED (Modified Separation of Cohesive Energy Density) [10], and HSP i.e. Hansen solubility parameter [11]: in some cases, the values are quite different indeed amongst the two sources, particularly for the linear alkanes. Consequently, it must be anticipated, that the outcome of the determination of the solubility parameter for the EPDM sample will be different, depending on which of the two sources are employed.

Table 12. Volume fractions of polymer in swollen mass (own investigation), molar volumes and solubility parameters of swelling agents: hydrocarbons at 22 °C
Tabela 12. Pęcznienie objętościowe elastomeru (badania własne), objętości molowe i parametry rozpuszczalności rozpuszczalników węglowodorowych w temp. 22 °C

Liquid	v_r [-]	v_s [cm³/mol]	δ_s [MPa$^{1/2}$] MOSCED [10]	δ_s [MPa$^{1/2}$] HSP [11]
hexane	0.26	130.8	15.70	14.90
decane	0.25	194.9	16.50	15.70
dodecane	0.25	227.1	16.70	16.00
cyclopentane	0.20	93.3	16.40	16.50
cyclohexane	0.19	108.1	16.80	16.80
cyclooctane	0.18	134.5	17.50	17.50
o-xylene	0.23	120.8	18.10	18.10
toluene	0.26	106.3	17.80	18.16

By the Flory–Rehner equation the relationship between the volume fraction of polymer in the swollen state: v_r as measured, and four component related parameters is defined. Values for the molar volume V_s and the solubility parameters of the liquids δ_s, can be taken from literature [10, 11], choosing either for

MOSCED or for HSP. The only two unknown parameters that remain then are: the solubility parameter of the EPDM-polymer δ_r, and the concentration of elastically active chains per unit volume, v_e.

To calculate for each of the rubber-solvent combinations the value of the number of elastically active chains per unit volume v_e, a range of values of δ_r was created and for each rubber-solvent system with the measured volume fraction of polymer in the swollen mass v_r, these were inserted in the Flory–Rehner equation. An exemplary equation for the cyclooctane case is presented hereunder:

$$v_e = \frac{\ln(1-0.184)-0.184-\left(0.34+\frac{(17.50-\delta_r)^2 \cdot 134.5}{8.32 \cdot 295}\right) \cdot 0.184^2}{134.5 \cdot \left(0.184^{\frac{1}{3}} - \frac{0.184}{2}\right)} \quad (33)$$

Different results from the different approaches to the problem were obtained. If for example swelling in toluene according to reference method [19] is considered, where the Flory–Huggins interaction parameter for the EPDM/toluene system is taken as $X_{EPDM/toluene} = 0.49$, and this used to calculate the crosslink density from the Flory–Rehner equation, a crosslink density $v_e = 1.49 \cdot 10^{-4}$ [mol/cm³] is obtained. If in that case the solubility parameter of toluene is taken from MOSCED: $\delta_{toluene\ MOSCED} = 17.80$ [MPa$^{1/2}$], the solubility parameter of the EPDM-rubber is equal to $\delta_r = 15.94$ [MPa$^{1/2}$]; respectively, $\delta_r = 16.30$ [MPa$^{1/2}$] when the Hansen Solubility Parameter $\delta_{toluene\ HSP} = 18.16$ [MPa$^{1/2}$] is employed. Those results do not correspond with data from the swelling tests in cycloalkanes, because the solvents mass uptake increases with rise in molar volume of the solvent and the solubility parameter. This indicates that the solubility parameter of the present EPDM-rubber must be higher than the solubility parameter of cyclooctane: $\delta_{cyclooctane} = 17.50$ [MPa$^{1/2}$]. Consequently, further investigation is necessary.

5.4.A. Accurate determination of the solubility parameter of EPDM rubber based on MOSCED [10]

The starting point is the solubility parameters of the various swelling liquids as determined by MOSCED and shown in Table 12. From each EPDM-liquid system considered, the swelling of the EPDM is largest in cyclooctane with $\delta_{sMOSCED} = 17.5$ [MPa$^{1/2}$]. It is thus expected that the solubility parameter of the investigated EPDM is close to this value. For the set of data the corresponding concentrations of active chains, v_e, were calculated with stepwise increase of δ_r from 16.0 to 18.0 [MPa$^{1/2}$], and can be plotted as shown in Figure 10. By plotting all results in one graph, it would be possible to assign an intersection point which corresponds with the solubility parameter of the rubber. This produces graphically represented four lines determined for the swelling tests in alkanes for example.
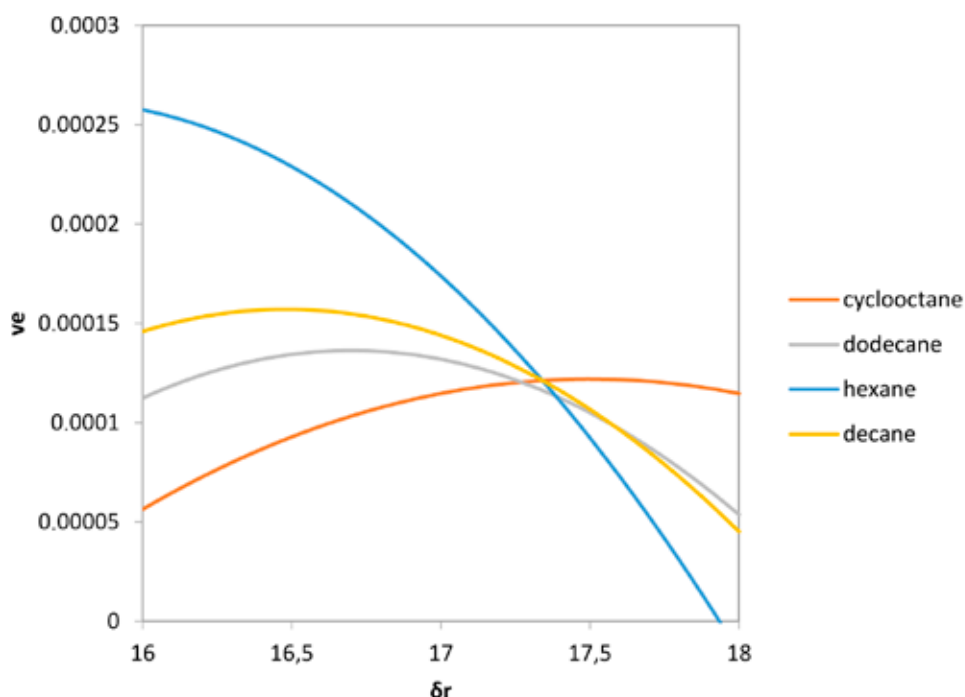

Fig. 10. Determination of solubility parameter of rubber δ_r by the intersection method, based on values of the solubility parameters of solvents taken from MOSCED [10]

Rys. 10. Wyznaczanie parametru rozpuszczalności kauczuku δ_r metodą przecięcia, z wykorzystaniem parametrów rozpuszczalności rozpuszczalników obliczonych wg metody MOSCED [10]

The lines from the alkanes intersect in one area but not at one point. In order to achieve one desired point of intersection, a trial-and-error method was used to establish one intersection point by slightly adjusting the solubility parameters for the four solvents considered: Table 13, with Figure 11 as a result. Very minor adjustments were needed for this. However, inserting the data for the aromatic solvents toluene and *o*-xylene herein, Figure 12, leads to large deviations again. It shows that the solubility parameters taken from literature for these liquids are useless in this case and that further fitting needs to be done. Indeed, quite large adjustments of the solubility parameters for these solvents are needed compared to the MOSCED data, as shown again in Table 13.

From this investigation, the estimated solubility parameter of the EPDM-rubber and crosslink density are set as δ_r = 17.34 [MPa$^{1/2}$] and v_e = 1.29 · 10^{-4} [mol/cm^3].

Table 13. Comparison of the solubility parameters of solvents used in determination of the solubility parameter of rubber according to MOSCED [10]

Tabela 13. Porównanie parametrów rozpuszczalności rozpuszczalników, obliczonych wg metody MOSCED [10], wykorzystanych do oznaczania parametrów rozpuszczalności kauczuku

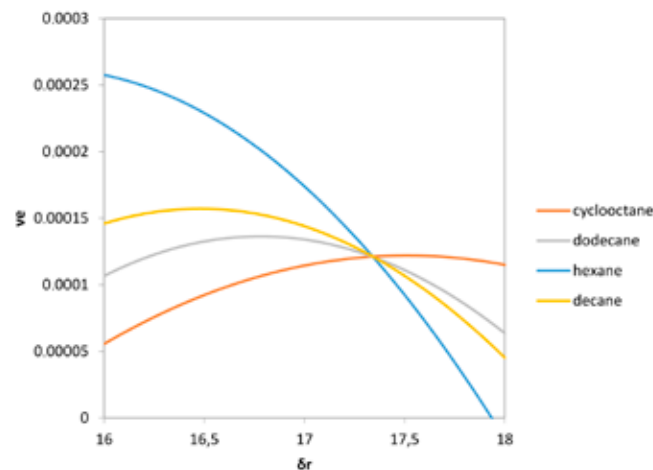| Solvent	Taken from literature (MOSCED [10])	Adjusted
	δ_s [MPa$^{1/2}$]	
hexane	15.70	15.74
decane	16.50	16.54
dodecane	16.70	16.62
cyclooctane	17.50	17.50
toluene	17.80	19.30
o-xylene	18.10	18.90

Fig. 11. Determination of solubility parameter of rubber δ_r by the intersection method based on adjusted values of the solubility parameters of solvents taken from MOSCED [10] with slight adjustments

Rys. 11. Wyznaczanie parametru rozpuszczalności kauczuku δ_r metodą przecięcia na podstawie parametrów rozpuszczalności rozpuszczalników obliczonych wg MOSCED [10], z nieznacznym dopasowaniem
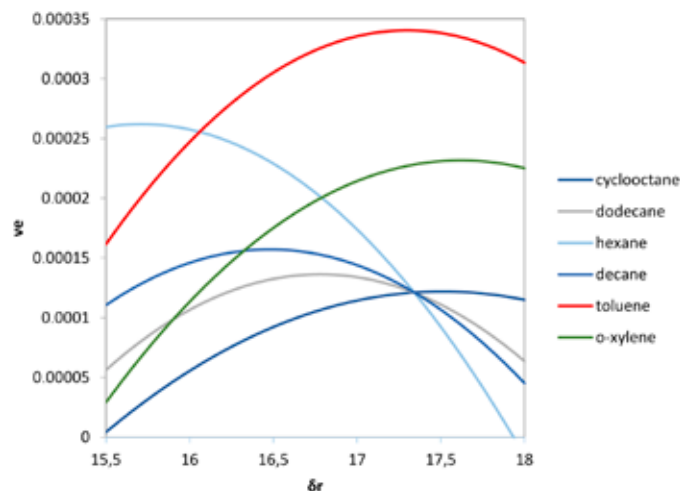

Fig. 12. Determination of solubility parameter of rubber δ_r by the intersection method based on slightly adjusted values of solubility parameters of solvents taken from MOSCED [10], with additional data for aromatic solvents

Rys. 12. Wyznaczanie parametru rozpuszczalności kauczuku δ_r metodą przecięcia na podstawie parametrów rozpuszczalności rozpuszczalników obliczonych wg metody MOSCED [10], z dodatkowymi danymi dla rozpuszczalników aromatycznych

Another approach to this problem is presented in Figure 14, wherein the data taken only from cycloalkanes are considered, because for those liquids the solvent mass uptakes are the largest. Consequently, it suggests a better correlation of the solubility parameters of the EPDM-rubber and solvenst. The solubility parameter of the rubber obtained from the intersection method in this case reads δ_r = 17.86 [MPa$^{1/2}$] with crosslink density v_e = 1.28 · 10^{-4} [mol/cm^3], without additional fitting. This value of the solubility parameter of the EPDM-rubber seems to be more accurate and probable, at least as far as based on the MOSCED [10] data.
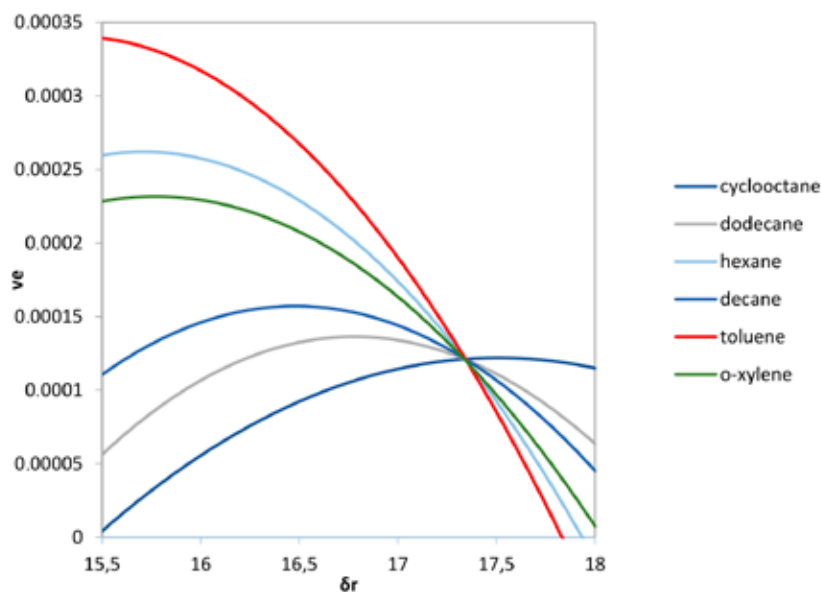

Figure 13. Determination of the solubility parameter of rubber δ_r by the intersection method based on values of the solubility parameters of solvents taken from MOSCED [10] with additional fitting and data for aromatic solvents
Rys. 13. Wyznaczanie parametru rozpuszczalności kauczuku δ_r metodą przecięcia na podstawie parametrów rozpuszczalności rozpuszczalników obliczonych wg metody MOSCED [10], z dodatkowym dopasowaniem i danymi dla rozpuszczalników aromatycznych
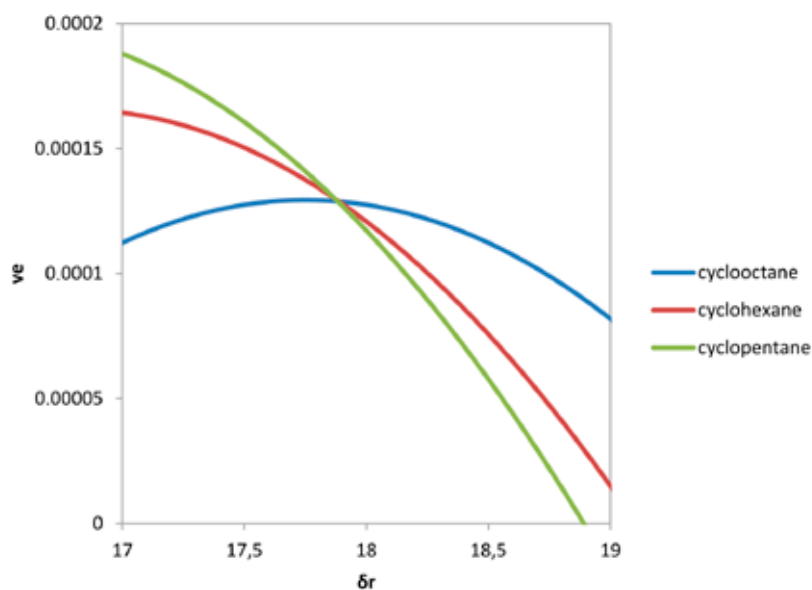

Fig. 14. Determination of the solubility parameter of rubber δ_r by the intersection method based on values of solubility parameters of cycloalkanes taken from MOSCED [10]
Rys. 14. Wyznaczanie parametru rozpuszczalności kauczuku δ_r metodą przecięcia na podstawie parametrów rozpuszczalności cykloalkanów obliczonych wg metody MOSCED [10]

5.4.B. Determination of the solubility parameter of EPDM rubber based on HSP [11]

If the values of the Hansen solubility parameters for alkanes are considered, it is seen that those values are much lower than those from the MOSCED database. The solubility parameter of the EPDM-rubber from the alkanes swelling data is obtained as δ_r = 16.54 [MPa$^{1/2}$], with crosslink density v_e = 1.23 · 10^{-4} [mol/cm^3], as shown in Figure 15. That value is possible only when the solubility parameter of cyclooctane is largely changed to $\delta_{cyclooctane}$ =16.55 [MPa$^{1/2}$]: Table 14, so close to the solubility parameter of the rubber.

It proves that the solubility parameter of the EPDM-rubber is close to the one of cyclohexane, but application of the Flory-Rehner equation in the determination of the solubility parameter of the rubber is very sensitive to small changes in volume of solvent adsorbed by the rubber, what can totally change the results of the investigation. Most reasonable in this context is therefore to use data of

swelling tests in mixtures of solvents and to compare the changes in solubility parameters of the solvents with the mass changes at equilibrium swelling.

Table 14. Comparison of the solubility parameters of solvents used in determination of solubility parameter of rubber according to HSP [11]

Tabela 14. Porównanie parametrów rozpuszczalności rozpuszczalników, obliczonych wg metody HSP [11], wykorzystanych do oznaczania parametru rozpuszczalności kauczuków

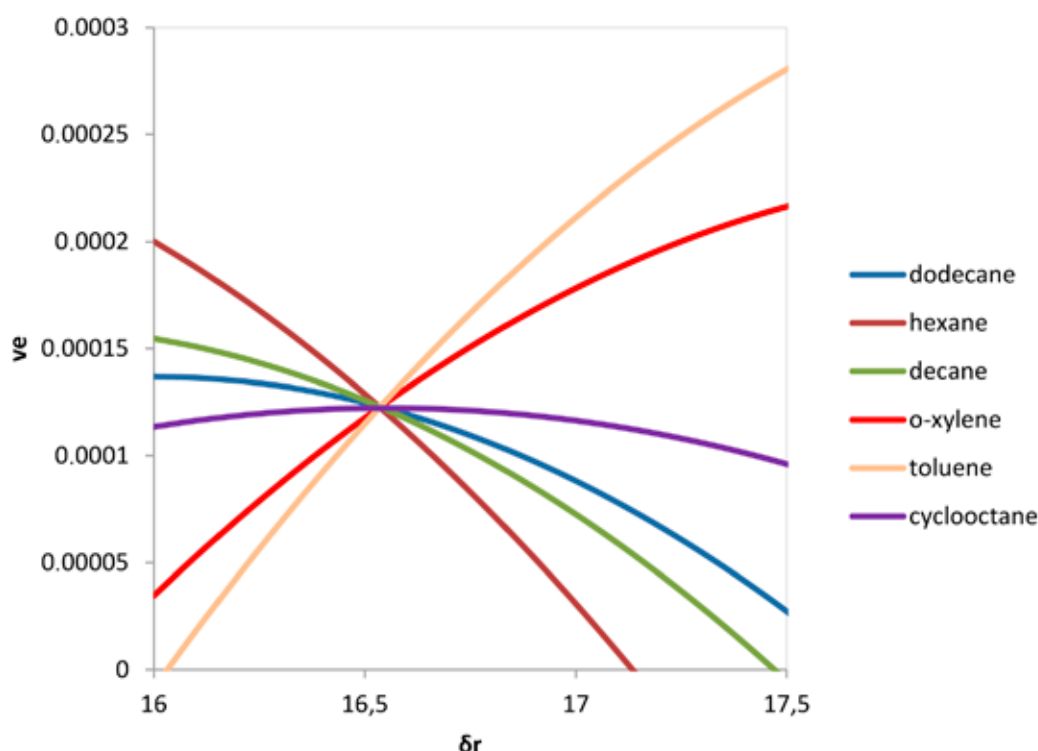| Solvent	Taken from literature (HSP [11])	Adjusted
	δ_s [MPa$^{1/2}$]	
hexane	14.90	14.90
decane	15.70	15.66
dodecane	16.00	16.00
cyclooctane	17.50	16.55
toluene	18.16	18.52
o-xylene	18.10	18.10

Fig. 15. Determination of the solubility parameter of rubber δ_r by intersection method based on values of solubility of solvents taken from HSP [11] with additional fitting and data from alkanes and aromatics

Rys. 15. Wyznaczanie parametru rozpuszczalności kauczuku δ_r metodą przecięcia na podstawie parametrów rozpuszczalności rozpuszczalników obliczonych wg metody HSP [11], z dodatkowym dopasowaniem i danymi dla alkanów i związków aromatycznych

5.4.C. Determination of EPDM solubility parameter based on swelling tests in mixtures of solvent

Because the Hansen solubility parameter seem to be more accurate, as shown in Table 14, swelling experiments for pure solvents and mixtures were compared with the Hansen solubility parameter: Table 15. From this investigation, it is clearly seen that the highest mass uptake is given for mixture number X: 25% of *o*-xylene and 75% of cyclooctane, and it seems to be equal to the solubility of rubber. It seems to indicate a solubility parameter for the EPDM-rubber of δ_r = 17.65 [MPa$^\frac{1}{2}$], the more because the mass change for mixtures number II and VII, the same distance of above and below the $\delta_s - \delta_r$ is the same. It gives information that using the Hansen Solubility Parameter data is the best way of predicting the solubility of EPDM-rubber and the solvents among the methods considered here.

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Table 15. Mass fractions of solvents in mixtures, mass changes of EPDM vulcanizates by mixed solvents uptake, average solubility parameters calculated according HSP [11] for 3 pure solvents and mixtures of *o*-xylene, cyclooctane and dodecane (room temperature)
Tabela 15. Pęcznienie wagowe wulkanizatów EPDM w mieszaninie rozpuszczalników, średnia wartość parametrów rozpuszczalności, obliczonych metodą HSP [11], rozpuszczalników: *o*-ksylenu, cyklooktanu i dodekanu oraz ich mieszaniny (temp. pokojowa)

Mixture number	*o*-xylene [wt. %]	cyclooctane [wt. %]	dodecane [wt. %]	mass change [wt. %]	HSP δ_s at 20 °C [MPa$^{1/2}$]	$\delta_s - \delta_r$ at 20 °C
I	100	0	0	**310**	18.10	0.45
II	0	100	0	**400**	**17.50**	−0.15
III	0	0	100	**250**	16.00	−1.65
IV	33	33	33	**330**	17.03	−0.62
V	75	25	0	**370**	17.95	0.30
VI	75	0	25	**330**	17.58	−0.07
VII	50	50	0	**400**	**17.80**	0.15
VIII	50	0	50	**310**	17.05	−0.60
IX	0	50	50	**330**	16.75	−0.90
X	25	75	0	**420**	**17.65**	0.00
XI	25	0	75	**290**	16.53	−1.13
XII	0	75	25	**370**	17.13	−0.52
XIII	0	25	75	**290**	16.38	−1.28
XIV	50	25	25	**360**	17.43	−0.22
XV	25	50	25	**350**	17.28	−0.38
XVI	25	25	50	**320**	16.90	−0.75

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